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Calorimetric Properties of Diphenyl Ether From 0° to 570°K

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The heat capacity, enthalpy, and entropy of diphenyl ether from 0° to 570° K are calculated from experimental heat capacities obtained by using an adiabatic vacuum calorimeter and a Bunsen ice calorimeter. The heat of fusion and the triple-point temperature are given as 17,216 ±17 absolute joules mole^{-1} and 300.03 ±0.01° K, respectively. Heat of combustion experiments in a bomb calorimeter gave the value −6,135.64 ±0.88 absolute kilojoules mole^{-1} for the standard heat of combustion of the liquid at 30° C. The standard heats of combustion and formation are computed for both liquid and solid at 25° C. The standard entropy and Gibbs free energy of formation for the solid at 25° C are given as −590.1 ±0.5 absolute joules deg^{-1} mole^{-1} and 143.8 ±0.9 absolute kilojoules mole^{-1}, respectively.

I. Introduction

Frequently in calorimetry it is desirable to have access to standard substances whose thermal properties are accurately known to calibrate and test calorimeters under conditions of actual use. Water has been used quite extensively as a standard substance in heat capacity and latent heat of vaporization calorimeters, but it has a relatively limited temperature range of application due to its rather rapid vapor pressure increase above 100° C and its large change in volume on freezing. Often the choice of a standard is dictated by the calorimeter design, consequently there should be a number of standards from which to select the most suited. In heat-capacity calorimetry, as well as in other types of calorimetry, the basic requirements for any standard substance are high chemical stability; high purity, which can be attained and retained easily; reproducibility of physical state; and easy manipulation in the calorimetric apparatus. It is advisable to test heat capacity calorimeters under conditions such that the heat capacity of the calorimetric system is closely the same whether it contains the standard material or the test material. If a standard of high heat capacity per unit volume is available, this condition can be met easily by adjusting its quantity in the calorimeter.

Diphenyl ether has been known to be relatively stable and to be obtainable in a high state of purity by fractional distillation followed by crystallization. As this material melts close to room temperature, it is being developed at this Bureau for use in triple-point cells, as a thermostatic medium at its melting point and in a modified Bunsen calorimeter. The accurate measurement of the thermal properties of diphenyl ether is desirable for these applications as well as for improvement in design of high-temperature heat-transfer equipment in which diphenyl ether is being used in the form of diphenyl-diphenyl ether eutectic mixture.

The heat capacity of diphenyl ether was measured between 18° and 573° K, using two calorimeters widely different in design. An adiabatic vacuum calorimeter was used from 18° to 360° K, and a "drop" method was used from 273° to 573° K with an accurately thermostated furnace and an improved Bunsen ice calorimeter. The two methods overlap in the temperature range between 273° to 360° K, where they serve to check each other. The triple point and heat of fusion were measured in the adiabatic vacuum calorimeter. An isothermal jacket water calorimeter was used for the determination of heat of combustion.

II. Low-Temperature Calorimetry

1. Apparatus

The melting-point studies and heat-capacity measurements from 18° to 360° K were made with an adiabatic vacuum-type calorimeter essentially the same as that described in the paper on 1,3-butadiene by Scott, et al [1].[1] Briefly, the apparatus and procedure were as follows. The diphenyl ether, freed of air and water, was sealed in a copper container, which in turn was suspended inside an evacuated adiabatic shield system. The copper sample container had a volume of about 60 ml and was provided with a central well for a thermometer and heater. For rapid dissipation of heat to the sample, copper vanes radiated out from this well. No part of the sample was more than 2 mm from the copper vanes. A thin coating of pure tin was applied to the inner surfaces of the container to provide an inert surface to the sample and to solder the vanes in place. The outer surface of the container, as well as the adjacent surface of the adiabatic shield, were polished to cut down the effect of heat transfer by radiation. The heat transfer by convection was made negligible by pumping the vacuum space to 10^{-5} mm Hg or better. During an experiment the shield temperature was kept, at all times, equal to that of the sample container surface by controlling the shield heaters, using constantan-chromel *P* thermels to integrate surface temperatures. One set of three-junction thermels and another of two-junction thermels were used. In the melting-point studies and heat-capacity experiments, the electrical energy introduced into the sample and container was determined by means of a precision potentiometer in conjunction with a volt box and a

[1] Figures in brackets indicate the literature references at the end of this paper.

standard resistor. The time was measured by using a precision interval timer operated on standard 60 cycles furnished by the Radio Section of this Bureau. This timer was compared periodically with time signals from the Time Section and found not to vary by more than 0.02 sec for any heating period, which was never less than 2 min. The initial and final temperatures of a heating interval were measured by means of a platinum resistance thermometer and a G–2 Mueller bridge. The platinum resistance thermometer was calibrated at this Bureau above 90° K on the International Temperature Scale [2] and between 10° to 90° K on a provisional scale [3], which consists of a set of platinum resistance thermometers calibrated against a gas thermometer. The resistance of the thermometer was frequently checked at the ice point, and the small fluctuations observed were too insignificant to affect the results of the measurements. The volt box, standard resistor, potentiometer, and bridge were calibrated recently at this Bureau.

2. Purity and Triple-Point Temperature

The diphenyl ether used in this investigation was purified by F. L. Howard of this Bureau by means of a fractional distillation followed by 25 fractional crystallizations. A portion of this diphenyl ether was treated by the following procedure in order to remove the dissolved air and water. The material was slowly frozen in a glass bulb during evacuation; then after melting, this process was repeated. After distilling the sample completely into a second bulb, the process of slow freezing while evacuating was repeated again. A portion (36.7724 g in vacuum) of this sample was transferred to the copper container by gravity, and the container was sealed with solder.

The purity of this air-free diphenyl ether was determined calorimetrically from the melting-point studies. In this method the equilibrium temperatures are measured at various increasing liquid-solid ratios as determined from the electric energy input, heat of fusion, and heat capacity of the system. The experimental data are treated on the assumption that Raoult's law is obeyed and no solid solution is formed in the concentration range under investigation. The simplified equation, $N_2=A\Delta T$, is used to represent the relation between mole fraction impurity, N_2, and the depression, ΔT, of the triple point. The cryoscopic constant, A, is calculated from $A=L_f/RT_t^2$, where L_f is the heat of fusion, R the gas constant and T_t the triple-point temperature. The observed equilibrium temperatures are plotted against $1/F$, the reciprocal of the fraction of material in the liquid state. This curve is extrapolated to $1/F=0$ to obtain the triple point of the pure substance, and the slope of this curve is multiplied by the cryoscopic constant to obtain mole fraction impurity.

The purity of diphenyl ether was determined before and after the heat-capacity measurements to ascertain whether any chemical change had taken place under the conditions inside the calorimeter

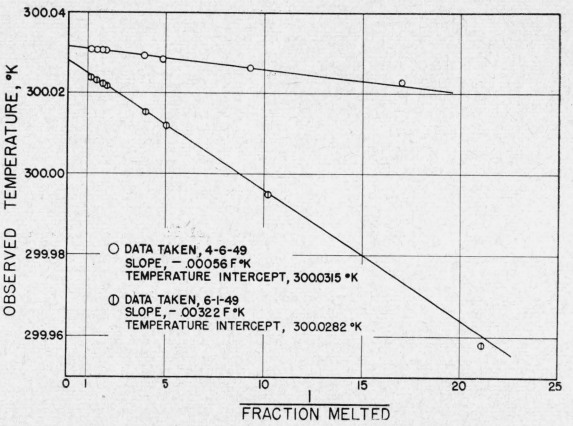


FIGURE 1. *Melting curves of diphenyl ether.*

sample container. Table 1 and figure 1 show the results of these measurements. Although the inside of the container is completely covered with pure tin, which is considered to be inert, the results show that the liquid soluble-solid insoluble impurity has increased from 0.000013 to 0.000074 mole fraction. This is rather surprising compared to only 0.00002 mole fraction increase indicated in the high-temperature measurements mentioned in a later section. Perhaps the inner surface of the sample container used with the adiabatic calorimeter has a catalytic effect on the decomposition of diphenyl ether even as low as 360° K. As the absolute purity is still high, the impurities would have only a negligible influence on the heat capacities.

TABLE 1. *Melting points of diphenyl ether*

$N_2=0.0230\,\Delta T$

Before the heat-capacity measurements		
$1/F$	$T_{obs.}$	$T_{calc.}$
17. 01	300. 0231	300. 0219
9. 33	300. 0264	300. 0262
4. 90	300. 0285	300. 0287
3. 93	300. 0292	300. 0293
2. 01	300. 0308	300. 0304
1. 79	300. 0306	300. 0305
1. 50	300. 0306	300. 0307
1. 26	300. 0308	300. 0308
1. 00	--------	300. 0309
Temperature intercept, 300.0315°K. Impurity, 0.000013 mole fraction.		
After the heat-capacity measurements		
$1/F$	$T_{obs.}$	$T_{calc.}$
21. 11	299. 9581	299. 9603
10. 25	299. 9951	299. 9952
5. 03	300. 0122	300. 0118
4. 02	300. 0154	300. 0153
2. 00	300. 0219	300. 0217
1. 79	300. 0223	300. 0229
1. 50	300. 0231	300. 0234
1. 27	300. 0240	300. 0241
1. 00	--------	300. 0250
Temperature intercept, 300.0282°K. Impurity, 0.000074 mole fraction.		

The difference in the two temperature intercepts, 300.0315° and 300.0282° K,[2] amounting to 3.3 mdeg is believed to have been caused by small changes in the resistance thermometer and bridge between periods of the measurements. This change, however, does not affect the slope of the melting curve, as it only causes a parallel displacement in temperature. For a given set of measurements the temperatures agreed to within a few tenths of a millidegree. Considering the calibration uncertainties in the bridge and platinum resistance thermometer and uncertainty in the absolute temperature scale, the triple point of diphenyl ether is taken to be 300.03±0.01° K.

The third column of table 1 gives temperatures obtained from the equation $T_t - T_{calc} = N_2/AF$. Here N_2 is the mole fraction impurity calculated from the experimental data. The relation between the results in the second and third columns shows that Raoult's law was followed quite closely. The value of the cryoscopic constant A used in all the calculations is 0.0230 deg^{-1}.

3. Heat of Fusion

The latent heat of fusion of diphenyl ether was determined by adding electric energy continuously from a temperature a few degrees below the triple point to a temperature above the triple point. The quantity of energy was corrected for the heat capacity of the material plus the container on both sides of the triple point and for a small amount of premelting caused by the presence of impurities. The heat of fusion was determined soon after the first purity measurements, thus the premelting corrections have been calculated on the basis of 0.000013 mole fraction impurity. The results and corrections are tabulated in table 2. $\int CdT$ is the sum of the heat capacity corrections above and below the triple point. The mean value obtained for three determinations is 17,216 abs j $mole^{-1}$, and the mean deviation is ±2 abs j $mole^{-1}$. Considering the arbitrariness involved in the heat-capacity correction a probable error[3] of ±0.1 percent is assigned. The value for the heat of fusion is taken as 17,216 ±17 abs j $mole^{-1}$.

TABLE 2. *Heat of fusion of diphenyl ether*

Mole weight, 170.20 g; mass of sample, 36.7724 g

Defined calorie=4.1840 abs j.

Temperature interval	Total energy	$\int CdT$	Premelting correction	L_f
°K	*abs j*	*abs j*	*abs j*	*abs j*
298.4668 to 305.2408	4357.49	639.47	1.34	3719.36
296.1288 to 303.6634	4404.12	685.48	0.54	3719.18
295.5214 to 303.0956	4401.96	682.00	.30	3720.26
Mean				3719.60
Mean deviation				±0.44

Heat of fusion $\begin{cases} 101.152 \pm 0.012^a \text{ abs j } g^{-1} \\ 17,216 \quad \pm 2^a \quad \text{abs j mole}^{-1} \end{cases}$

[a] These values are mean deviations.

4. Heat Capacity

The heat capacity of the diphenyl ether sample (36.7724 g mass) plus the container was measured from 18° to 360° K in the adiabatic vacuum calorimeter. Between 18° and 80° K solid and liquid hydrogen were used to cool the material and above 80° K liquid air, solid carbon dioxide, and ice were used. During heat-capacity experiments in the temperature range 18° to 30° K, where the heat-capacity curve changes rapidly in slope, the temperature change per heating interval was about 2 deg. The interval was increased to 4 or 5 deg up to 100° K, and above this temperature intervals of 6 to 10 degrees were used.

Nine series of experiments were made on the full container in the solid range, and the temperature ranges covered were 20° to 98° K, 15° to 29° K, 13° to 100° K, 88° to 234° K, 215° to 295° K, 125° to 295° K, 105° to 216° K, 90° to 105° K, and 101° to 205° K. Five series of experiments in the liquid range consisted of the following temperature ranges: 302° to 367° K, 304° to 370° K, 305° to 367° K, 303° to 320° K, and 321° to 348° K. Six series of experiments were made on the empty container, and the temperature ranges were 13° to 35° K, 15° to 31° K, 28° to 60° K, 90° to 370° K, 50° to 119° K, and 279° to 342° K. Curvature corrections were applied to these measurements wherever significant, using the relation given by Osborne, et al. [4]:

$$Z_{T_m} = Q/\Delta T - \left(\frac{\partial^2 Z}{\partial T^2}\right)_{T_m} \frac{\Delta T^2}{24} \cdots \qquad (1)$$

Z_{T_m} is the corrected heat capacity at the mean temperature, T_m, of the interval ΔT; Q is the electrical energy added; and $(\partial^2 Z/\partial T^2)_{T_m}$ is the second derivative of the heat capacity with respect to temperature at T_m. The observed results (corrected for curvature) were plotted on a large scale as deviations from an approximate empirical equation and a smooth curve was drawn through the deviation points. The smooth deviation curve and the empirical equation were then used to obtain smoothed heat capacities at equally spaced integral temperatures. Similar heat-capacity experiments were made with the empty container, and the results were treated in the same manner. The weight of the container was different for the experiments with and without the sample. This arose from small differences in the weights of the copper filling tube and solder for the two experiments. Corrections for these differences in weights were applied to the smoothed heat capacities for the empty container from known heat capacities of copper and solder. The deviations of experimental

[2] All temperatures expressed in degrees Kelvin were obtained from the relation °K=°C+273.1600.

[3] For these experiments a true probable error cannot be statistically computed. The values given are estimates arrived at by examining contributions to the inaccuracy from all known sources, and they are to be considered (unless stated otherwise) as the authors' best estimate of the error, which is just as likely to be exceeded as not.

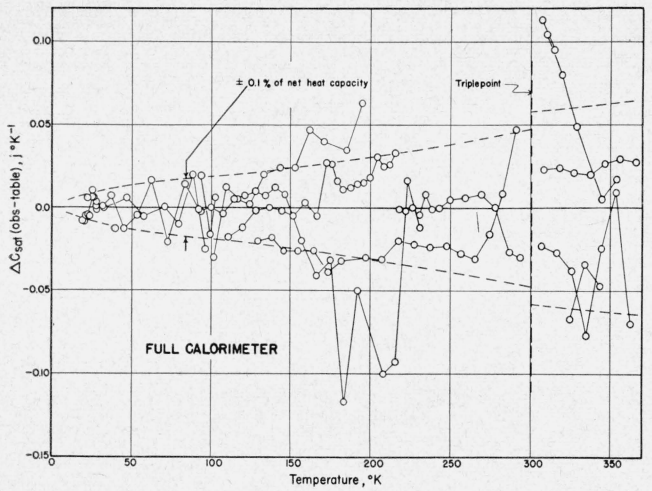


FIGURE 2. *Deviations of experimental heat capacities (corrected for curvature) from smoothed values for the container plus diphenyl ether.*

The experiments in a single series of measurements are connected by lines.

heat capacities from the smoothed values for the full and empty container are shown in figures 2 and 3. Most of the points lie within 0.1 percent of the net heat capacity. The net heat capacities were calculated, using the equation given by Hoge [5],

$$C_{\text{sat.}}=\frac{Z_2-Z_1-T\frac{d}{dT}\left[\frac{dp}{dT}(V-mv_c)\right]}{m/M}, \tag{2}$$

where Z_2 and Z_1 are the tabulated heat capacities for the full and empty container, respectively, at the same temperature T; p is the vapor pressure; m is the mass of sample; M is the molecular weight of diphenyl ether; V is the volume of the container; and v_c is the specific volume of the condensed phase. The term involving the vapor correction was not actually used, for it does not contribute significantly to the results obtained with the low-temperature adiabatic calorimeter. At 360° K this vapor correction amounts to only 0.002 percent. The values of heat capacity listed in table 4 from 18° to 300° K are those obtained from these calculations. The heat-capacity values below 18° K in this table were obtained by extrapolation, using the Debye equation,

$$C_{\text{sat.}}=59.91D\left(\frac{112}{T}\right), \tag{3}$$

fitted to the heat capacity at 18°, 20°, and 22° K. The values tabulated between 300° and 360° K were obtained by adjusting the slight differences between the results with the low-temperature adiabatic calorimeter and the ice calorimeter. The method of adjustment is discussed in a later section.

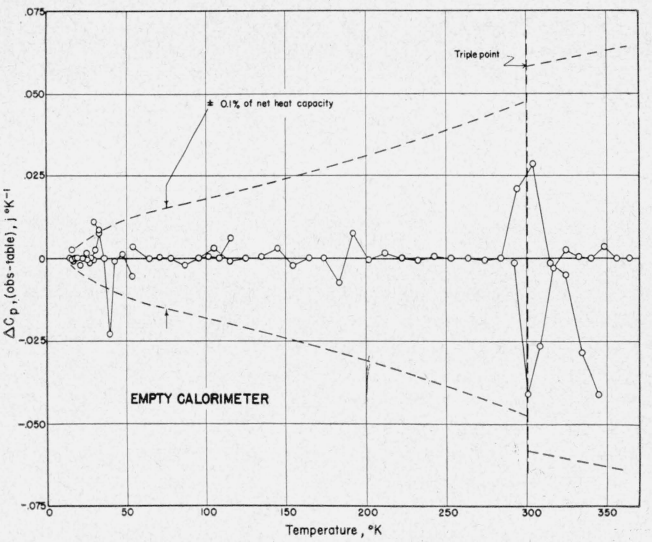


FIGURE 3. *Deviations of experimental heat capacities (corrected for curvature) from smoothed values for the empty container.*

The experiments in a single series of measurements are connected by lines.

5. Reliability of Heat-Capacity Results Obtained With the Low-Temperature Adiabatic Calorimeter

The precision of the heat-capacity experiments is shown in figures 2 and 3 of the previous section, in which the results (corrected for curvature) of the individual measurements are plotted as deviations from smoothed heat-capacity values for sample plus container and for container alone. As the experiments were made over a wide temperature range instead of a series of experiments over the same temperature interval, it is believed that a statement of average deviation is misleading in this situation. The conditions, particularly the heating rate, in the calorimeter were made as close as possible in the two series of experiments, so that certain systematic additive errors would cancel out. As a further check, the heat-capacity experiments were made at heating rates of 0.9 and 1.5 deg/min. Under these conditions large heat leaks dependent upon heating rate should be detectable, but the results obtained with the two heating rates showed no obvious differences on the large-scale deviation plot. In the two sets of measurements, although precaution was taken to install the sample container in the same position within the adiabatic shield system, it is possible that there were some differences in the positioning of the thermels and leads. Any error from this source is indeterminate, but it is believed that the probable error is not greater than ± 0.05 percent.

The effect of impurities on the heat-capacity results is considered to be negligible.

Upon consideration of the above uncertainties the probable error of ± 0.2 percent is assigned to the heat-capacity values above 50° K in table 4. Below 50° K the accuracy is less, increasing to about 1 percent at 18° K.

III. High-Temperature Calorimetry

1. Method and Apparatus

The enthalpy measurements at higher temperatures, which supplement the heat-capacity measurements made from 18° to 360° K, covered the range 273° to 573° K (0° to 300° C). These were carried out by essentially the same method and apparatus as used previously in measurements on sodium up to 900° C [6]. In brief, the method is as follows. The sample, sealed in its container, is suspended in a furnace until it comes to the chosen constant temperature, as measured by a platinum resistance thermometer. It is then dropped into a Bunsen ice calorimeter, which measures the heat evolved by the sample plus container in cooling to 0° C. A similar experiment is made with the empty container at the same temperature. The change in enthalpy of the sample between 0° C and the temperature in the furnace is computed from the difference in the two values of heat. The heat capacity can be derived from enthalpy values of the sample so determined for a series of temperatures.

The sample was taken from the same supply as that used in the low-temperature measurements. A sample of about 8 g of the solid was melted and transferred to a monel container (volume, about 11 ml), which was similar to the container used in earlier measurements on *p*-xylene [7]. In order to remove most of the air and water in the sample, the container was heated to about 100° C while evacuating the space above the sample. The method of sealing the container while still evacuating is shown in figure 4. One end of the container is made with a threaded projection, which can be temporarily sealed to a connecting fitting by means of a tin gasket, *C*. The container can be evacuated and filled through the filling tube, *B*. The actual sealing of the container is at the gold gasket, *D*, which is attached to the bottom end of the monel screw insert. Rotation of the screw insert for sealing is accomplished by the screw driver, *A*, which is sealed from the atmosphere by a packing not shown. In this way, it is possible to retain all the advantages of a valve with a packing, but reduce the mass and thereby the heat capacity, of the sealed container to a minimum. Also, the mass of the metal container is definite and not dependent on a soldered seal, as in the low temperature adiabatic calorimeter.

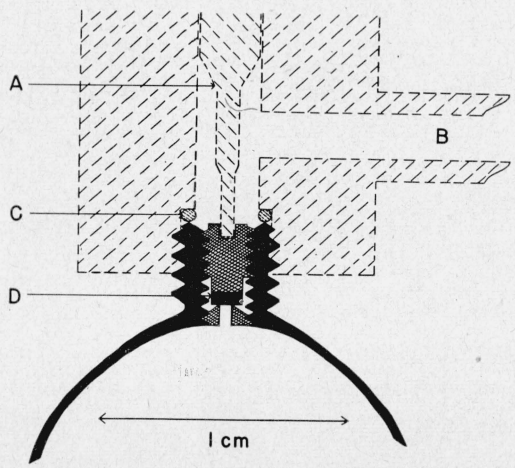


FIGURE 4. *Filling device and the seal for the capsule.*

A, Screw driver; B, filling tube; C, tin gasket; D, gold gasket.

2. Results

The results of the individual experiments are given in columns 2 and 3 of table 3. The measured heats listed are obtained from the mass of mercury drawn into the ice calorimeter, using the calorimeter calibration factor [6] of 270.46 abs j/g of mercury.

About 100 measurements were made, of which 56 were made with 7.8152 g (in vacuum) of sample in the container and the remainder with the empty container. The diphenyl ether was found to be solidified at 0° C in all experiments. Hence, every enthalpy calculated from a drop experiment starting with the liquid includes the heat of fusion. The sample was initially in the liquid state in all experiments except a few at furnace temperatures of 25.00° and 26.60° C (just below the triple point). In these experiments, the sample was solidified by dropping into the ice calorimeter prior to holding the solid sample in the furnace. By also making experiments with the supercooled liquid at the same temperatures as with the solid, there was obtained by differences the heats of fusion of 17,059 and 17,071 abs j mole^{-1} at 25.00° and 26.60° C, respectively. Upon extrapolation to the triple point, 26.87° C, using the heat capacities of solid and liquid found with the low-temperature adiabatic vacuum calorimeter, these values yield respectively 17,154 and 17,085 for the heat of fusion at the triple point. These values are lower by 0.3 and 0.7 percent, respectively, than the corresponding value of 17,216 abs j mole^{-1} found with the adiabatic calorimeter, and are considered much less reliable than the latter value. This is partly because of the small absolute uncertainty inherent in all measurements of heat by the ice calorimeter and partly because the sample used in the ice-calorimeter measurements was much smaller, so that a trace of impurity soluble in the diphenyl ether may have caused enough premelting at these temperatures to explain part of the discrepancy.

The difference between the measured heats for the empty container and the container with sample (columns 2 and 3 in table 3) gives essentially the enthalpy change in the sample between 0° C and the temperature involved. Actually, to get the true enthalpy change, this difference was corrected by an equation given by Osborne [8],

$$[Q]_1^2=[q-pV+mH+(V-mv)L/(v'-v)]_1^2, \qquad (4)$$

where $[Q]_1^2$ is the heat evolved in cooling a closed container in which there is a liquid in equilibrium with its vapor from temperature 2 to temperature 1;

TABLE 3. *Experimental results with the furnace and ice calorimeter*

Furnace temperature	Measured heat		[a] Enthalpy change of the $(C_6H_5)_2O$		
	Empty container	With $(C_6H_5)_2O$	Observed	Calculated from equation 5	Observed minus calculated
°C	*abs j*	*abs j*	*abs j mole*$^{-1}$	*abs j mole*$^{-1}$	*abs j mole*$^{-1}$
		[b] 366.8			
		[b] 367.4			
		[b] 367.9			
		370.1			
		368.9			
		368.4	5,146		
		366.7			
		368.3			
	132.8	368.1			
	132.5	368.2			
	131.8	368.2			
[c] 25.00 (solid)	131.9	368.6			
	131.6	1150.3			
	129.9	1151.0			
	132.1	1148.2			
	132.0	1150.1			
		1154.4			
		1150.0	22,206	22,209	−3
		1152.7			
		1149.9			
		1151.8			
[c] 25.00 (liquid)		1153.2			
		1153.5			
		1152.0			
		395.9			
		394.5			
		394.9			
[c] 26.60 (solid)		[d] 397.1			
		[d] 397.7			
		[d] 397.2			
		[d] 397.2			
[c] 26.60 (liquid)		1181.1			
		1179.4			
	[e](258.2)				
	262.3				
	264.2	1600.4			
	263.8	1597.5			
50.00	264.1	1598.9	29,078	29,042	+36
	263.5	1598.5			
	264.2				
	262.6				
	263.4				
	264.6				
	400.5				
	397.5				
75.00	398.1				
	[e](410.4)				
	399.2				
	535.2				
	535.0	2531.2			
	534.9	2531.0			
100.00	534.0	2536.0	43,484	43,548	−64
	536.8	2528.6			
	534.2				
	534.6				
	809.1	3528.7			
	809.1	3528.2			
150.00	810.1	3527.0	59,203	59,176	+27
	809.1	[e](3521.0)			
	1089.8	4578.6			
	1084.9	4574.5			
200.00	1092.3	4575.6	75,922	75,927	−5
	1089.2	4574.6			
	1089.7				
	1372.1	5687.6			
250.00	1374.0	5685.5	93,856	93,799	+57
	1373.4	5681.2			
		5679.8			
	1660.4	6837.4			
300.00	1660.3	6837.2	112,754	112,794	−40
	1658.9	6837.8			

[a] The contribution from vaporization has been eliminated.
[b] Not included in the mean because for these experiments the diphenyl ether was frozen rapidly, using dry ice.
[c] State of the sample at the furnace temperature.
[d] Experiment made after the higher-temperature experiments. The preceding three experiments of this set were made before the diphenyl ether had been heated above 150° C.
[e] Rejected by Chauvenet's criterion.

q is the contribution to Q made by the empty container, shields, and suspension wire; p is the vapor pressure of the liquid; V is the volume of the container; m is the total mass of liquid and vapor; H is the enthalpy per unit mass of the "saturated" liquid (i. e., at pressure p); v' and v are the specific volumes of saturated vapor and liquid, respectively; and L is the enthalpy of vaporization per unit mass. The maximum value of each of the two correction terms that convert measured heats ($[Q-q]_1^2$) to get true enthalpy $[H]_1^2$ amounted to only 0.05 percent at the highest temperature, 300° C. The mean values of enthalpy listed in column 4 of table 3 have been corrected in this way and converted to molal basis.

The mean values of enthalpy of the liquid diphenyl ether at each temperature (26.87° to 300° C) were fitted by an equation whose constants were determined by least squares:

$$H_t(\text{liquid})-H_0(\text{solid})=15657.2+256.4649t+0.224409t^2, \qquad (5)$$

where $H_t(\text{liquid})-H_0(\text{solid})$ is the enthalpy difference in abs j mole^{-1} (mole wt=170.20) between the liquid at $t°$ and the solid at 0° C. In evaluating the constants, equal weight was given to values of enthalpy, and at each temperature a weighting factor was used to correspond to the number of determinations made at that temperature.[4] The values calculated from eq 5 are given in column 5 of table 3.

Values of $C_{\text{sat.}}$ the heat capacity of the "saturated" liquid (in equilibrium with its vapor), were calculated from the thermodynamic relation

$$C_{\text{sat.}}=\left(\frac{\partial H}{\partial T}\right)_{\text{sat.}}-V_{\text{sat.}}\left(\frac{dp}{dT}\right)_{\text{sat.}}, \qquad (6)$$

where $V_{\text{sat.}}$ is the molal volume of the liquid and p the vapor pressure. The values of $(\partial H/\partial T)_{\text{sat.}}$ were determined by differentiating eq 5. The maximum contribution of the last term in the temperature range studied is at 300° C, and amounts to 0.15 percent of the heat capacity. The values of heat capacity so calculated may be represented by the equation

$$C_{\text{sat.}}=0.448818(T-273.16)+256.4649-V_{\text{sat.}}\left(\frac{dp}{dT}\right)_{\text{sat.}}. \qquad (7)$$

The values of heat capacity listed in table 4 at temperatures of 370° K and above are those calculated from this equation.

[4] Actually, the weighting factor used was $(1/a+1/b)^{-1}$, where a and b are the number of runs on the empty and the filled container, respectively, as it is the difference between the enthalpies of these two, which determines the net enthalpy of the sample.

TABLE 4. *Heat capacity, enthalpy, and entropy of solid and liquid diphenyl ether at saturation pressures*

T	$C_{sat.}$	$(H_{sat.}-E_0^a)$	$(S_{sat.}-S_0)$
	SOLID		
° K	*abs j deg* $^{-1}$ *mole* $^{-1}$	*abs j mole* $^{-1}$	*abs j deg* $^{-1}$ *mole* $^{-1}$
2	0.027	0.014	0.009
4	.213	.213	.068
6	.718	1.077	.240
8	1.699	3.401	.567
10	3.283	8.272	1.105
12	5.497	16.952	1.889
14	8.272	30.670	2.941
16	11.52	50.413	4.255
18	14.91	76.845	5.807
20	18.06	109.83	7.542
22	21.17	149.08	9.409
24	24.29	194.54	11.386
26	27.33	246.11	13.451
28	30.30	303.81	15.585
30	33.16	367.29	17.769
32	35.88	436.39	19.998
34	38.48	510.77	22.262
36	40.95	590.25	24.526
38	43.28	674.50	26.806
40	45.44	763.18	29.087
42	47.45	856.11	31.351
44	49.34	952.95	33.597
46	51.13	1053.4	35.827
48	52.85	1157.4	38.040
50	54.53	1264.8	40.235
55	58.41	1547.3	45.614
60	61.92	1848.2	50.856
65	65.14	2166.0	55.928
70	68.11	2499.2	60.881
75	70.97	2846.9	65.663
80	73.77	3208.8	70.344
85	76.52	3584.6	74.888
90	79.19	3973.8	79.347
95	81.80	4376.4	83.704
100	84.35	4791.8	87.959
105	86.90	5219.9	92.129
110	89.49	5661.0	96.231
115	92.15	6115.0	100.28
120	94.82	6582.5	104.25
125	97.53	7063.3	108.18
130	100.26	7557.7	112.06
135	103.04	8066.0	115.89
140	105.88	8588.3	119.68
145	108.77	9124.9	123.46
150	111.72	9676.2	127.19
155	114.68	10243	130.90
160	117.64	10823	134.59
165	120.64	11419	138.25
170	123.70	12030	141.91
175	126.80	12656	145.54
180	129.98	13298	149.15
185	133.20	13956	152.75
190	136.45	14632	156.35
195	139.75	15321	159.94
200	143.09	16028	163.53
205	146.47	16751	167.10
210	149.88	17493	170.68
215	153.35	18251	174.23
220	156.86	19027	177.81
225	160.41	19820	181.37
230	164.00	20630	184.94
235	167.65	21459	188.50
240	171.32	22306	192.07
245	175.05	23173	195.65
250	178.83	24058	199.22
255	182.64	24962	202.79
260	186.49	25884	206.37
265	190.37	26825	209.96
270	194.25	27787	213.55
275	198.15	28769	217.16
280	202.04	29770	220.77
285	205.98	30789	224.38
290	209.94	31829	227.98
295	213.98	32888	231.61
298.16	216.56	33569	233.91
300	218.06	33969	235.25
300.032	218.25	33975	235.27

TABLE 4. *Heat capacity, enthalpy, and entropy of solid and liquid diphenyl ether at saturation pressures*—Continued

T	$C_{sat.}$	$(H_{sat.}-E_0^a)$	$(S_{sat.}-S_0)$
	LIQUID		
° K	*abs j deg* $^{-1}$ *mole* $^{-1}$	*abs j mole* $^{-1}$	*abs j deg* $^{-1}$ *mole* $^{-1}$
300.032	268.42	51188	292.61
310	272.71	53884	301.45
320	277.17	56634	310.18
330	281.71	59428	318.78
340	286.25	62268	327.25
350	290.79	65153	335.62
360	295.35	68084	343.87
370	299.90	71060	352.03
380	304.39	74082	360.08
390	308.86	77148	368.05
400	313.33	80259	375.93
410	317.89	83415	383.72
420	322.36	86617	391.43
430	326.84	89863	399.07
440	331.30	93155	406.64
450	335.77	96491	414.13
460	340.32	99872	421.56
470	344.71	103298	428.93
480	349.16	106769	436.23
490	353.60	110284	443.48
500	358.04	113845	450.66
510	362.48	117450	457.80
520	366.92	121100	464.88
530	371.35	124794	471.91
540	375.78	128534	478.89
550	380.19	132318	485.83
560	384.63	136148	492.72
570	389.05	140022	499.57

3. Reliability of Results With Ice Calorimeter

In order to check the over-all accuracy of operation of the apparatus, heat-capacity experiments were made at temperatures of 25° and 250° C with water sealed in the container. In these tests, it was convenient for comparison of the results to make two series of measurements similar to those described in the measurements with water [9]. One series was made with the container mostly full of water, while the other series was made with a small amount of water. The results of the experiments compare very favorably with the results of the earlier work [9] with an adiabatic calorimeter. The average heat capacity from 0° to 250° C, as measured with the present apparatus, is about 0.02 percent lower than that measured with the earlier apparatus, with a reproducibility of about ±0.02 percent. This is well within the accuracy of the earlier work. At 25° C the reproducibility of the present apparatus was relatively poor, giving a value of about ±0.14 percent for the average deviation of the mean. In spite of this, the measured average heat capacity from 0° to 25° C was only about 0.05 percent lower than the accepted accurate value [9].

The reliability of the results may be considered in two ways. First, there is the reproducibility or precision of the experiments. The average deviation of a single experiment from the mean at a given temperature was ±0.19 percent in the case of the empty containers and ±0.09 percent in the case of the containers with the sample. As the enthalpy of the sample was about two to three times as great

as that of the empty container, the larger deviations with the empty container are not so important. At a given temperature the calculated probable error of the mean of the net enthalpy of liquid diphenyl ether, referred to that of the solid at 0° C, is about 0.04 percent. This error is about the same at all furnace temperatures.

In addition to the reproducibility of the results, there must be considered the sources of systematic errors. Many such errors have already been considered in other measurements with this apparatus [10] and will not be reviewed here. The ice-point reading of the platinum resistance thermometer was frequently redetermined during the measurements. On the basis of the small changes thereby noted, small corrections were applied to the heat measurements for deviations from the nominal temperatures. As these corrections were always less than 0.01 percent of the heat measured, it is believed that errors in the temperature scale did not appreciably affect the values of heat capacity.

Another source of systematic error is the effect of impurity in the sample. The measurements with the low-temperature adiabatic calorimeter indicated that the impurities in the sample amounted to only about 0.000013 mole fraction. However, in these measurements, considerable effort was made to remove both air and water. In the measurements with the ice calorimeter, some solid sample was melted and quickly transferred to the sample container, which was heated while pumping before sealing the capsule. Under these conditions, it seems improbable that the impurities amounted to more than 0.00005 mole fraction, a value that may be neglected insofar as effect on the heat-capacity values reported. However, small impurities affect greatly the measurements on the heat of fusion where the enthalpy of the solid is measured at temperatures close to the triple point. For example, in the measurements at 26.60° C (triple point=26.87° C), the measurements with the ice calorimeter gave a value of the enthalpy of the solid that corresponded to a heat of fusion value about 0.7 percent lower than that obtained with the adiabatic calorimeter. This difference could be explained by an impurity of about 0.00005 mole fraction in the sample. It is believed that the heat of fusion value obtained with the adiabatic calorimeter is the more accurate value.

Another factor affecting the reliability of the results is the question of the chemical stability of the diphenyl ether at the higher temperatures. The rate of spontaneous decomposition of diphenyl ether at 300° C does not seem to have been estimated previously. As this is the highest temperature to which the sample was subjected, a number of enthalpy determinations were made on the solid at 26.60° C (0.27 deg below the triple point) before and after several hours of heating to the higher temperatures.

Considering only the mean results of these two sets, it appears that the apparent relative enthalpy was greater in the second set of experiments by 47 abs j $mole^{-1}$. This corresponds to 0.3 percent more of the sample melted. It can readily be shown that this would be caused by an increase in impurity of only 0.00002 mole fraction. Here again, this impurity would not affect the reliability of the heat-capacity results, although it would have some significance in the heat of fusion value calculated from the measurements on the solid at 26.60° C.

Another source of systematic error lies in the uncertainty in the mass of the sample. The mass of the empty container was 0.0033 g less during the experiments with the empty container than it was before introducing the sample. The mass of the sample was taken to be the difference in weight of the full container and the container after removing the sample. It is possible that some material other than the sample was removed in this process, in which case, an uncertainty of as large as 0.04 percent might exist in the mass of the sample. The other sources of error, such as temperature measurement, calorimeter calibration factor, variation in heat loss on dropping the sample from the furnace, and possible slightly inaccurate correction for condensation of vapor inside the container, are estimated each to contribute an uncertainty to the enthalpy and heat capacity of from 0.01 to 0.02 percent.

Considering these various sources of error, it is believed that the values of relative enthalpy represented by eq 5 have the probable error of ± 0.15 percent, except below 100° C, where the probable error must be considered greater. Similarly, it was estimated that the values of heat capacity of the liquid as determined by the ice calorimeter (eq 7) have the probable error of ± 0.25 percent, except near 25° and 300° C, where the course of the enthalpy curve is more uncertain.

IV. Tabulated Heat Capacities

In the temperature range 300° to 360° K, values of heat capacity are obtained with both the low-temperature adiabatic calorimeter and the ice calorimeter. The values, except between 300° and 320° K, are displaced almost parallel from each other, the displacement being about 0.45 abs j deg^{-1} $mole^{-1}$. This difference between the two sets of values, however, is smaller than the estimates of absolute error claimed with the two methods. The results with the two methods were adjusted so that continuity exists in the heat capacity curve between the overlap range and the range above 360° K. The problem of continuity at 300° K does not arise because the heat-capacity curve is discontinuous at the triple-point temperature (300.03° K). The results from the two methods were adjusted with the following considerations. The enthalpy experiments with the ice-calorimeter method decrease in sensitivity with approach to the ice point; furthermore, derivatives of the enthalpy equation become less accurate toward the end of the experimental temperature range. The shield control in the adiabatic vacuum calorimeter becomes a little unwieldy at higher temperatures, and at the same time heat transfer by radiation can be significant if any unknown thermal gradients exist in the calorimeter.

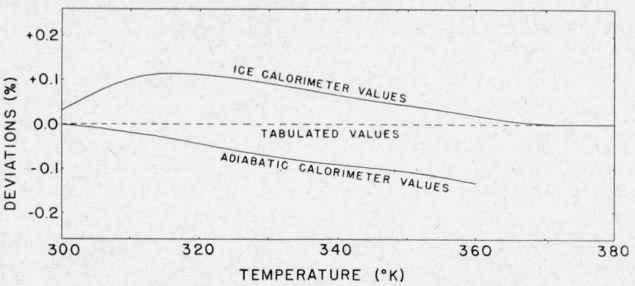


FIGURE 5. *Comparison of smoothed heat capacities obtained by the two experimental methods with the final values in table 4.*

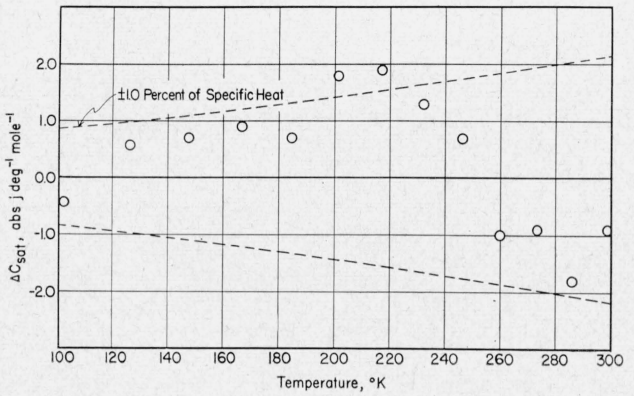


FIGURE 6. *Comparison of the values of heat capacity given in table 4 with the results of Smith and Andrews.*

The base line represents the values from the table.

The results from the ice calorimeter were given progressively greater weight toward 360° K and the results from the adiabatic vacuum calorimeter greater weight toward 300° K. A comparison of the results from these two calorimeters with the adjusted tabulated values from table 4 is given in figure 5, which shows that the maximum difference is about 0.13 percent.

The survey of literature revealed only one publication on the heat capacity of diphenyl ether. Smith and Andrews [11] measured the heat capacity from 100° to 300° K, using a heat conduction calorimeter. In figure 6 these results are compared with the tabulated values of table 4. In general, the values given by these authors are higher below 246° K and lower above this temperature. The over-all discrepancy amounts to about ±1 percent; the maximum discrepancy amounts to 1.2 percent. These authors claimed an accuracy of 1 percent for their apparatus.

V. Combustion Calorimetry

1. Apparatus and Procedure

The apparatus and procedure used in measuring the heat of combustion, with the exception of the Wheatstone bridge used in measurement of temperature, have been described in several previous publications [12, 13, 14]. The bridge used is a special Mueller type instrument with gold-chromium alloy resistance coils, which have negligible temperature coefficient of resistance so that the bridge does not need to be thermostated. The energy equivalent of the calorimetric system was determined by six experiments with NBS Standard Sample 39f, benzoic acid, using the value 26,433.8 abs j/g mass (weight in vacuum), previously obtained in this laboratory [15, 16, 17], for the heat of combustion of this substance under the standard conditions of the bomb process. The mean value obtained for the energy equivalent is 13,976.42 abs j deg^{-1}, and the standard deviation of the mean is ±0.64 abs j deg^{-1}. (See footnote a, table 5 for the definition of standard deviation.)

The observed heat of combustion in each experiment was corrected for the heat of stirring and the heat transfer between the jacket and calorimeter, for the energy used in firing the charge and for the energy of formation of nitric acid in the bomb. The observed values of the heat of combustion of diphenyl ether were reduced to $-\Delta U_C^\circ$ [18], the decrease in intrinsic energy accompanying the combustion reaction

$$C_{12}H_{10}O_{(l)}+14O_{2(g)}=12CO_{2(g)}+5H_2O_{(l)}$$

with the components in their thermodynamic standard states at 30° C. In the above reaction the standard state for diphenyl ether was taken as that of the liquid at 1-atm pressure.

Three combustion experiments were made with the samples of diphenyl ether in an open platinum crucible, and three with the samples enclosed in thin-walled glass bulbs [19, 20] flattened on opposite sides. The method for filling the bulbs is described in the references given. The weight of the glass in each bulb was about 0.05 g. There was no significant difference in the results obtained by the two methods.

The carbon dioxide formed in the combustion was absorbed in Ascarite and weighed, following the procedure described by Prosen and Rossini [21]. The absorption train, however, did not contain any provision to oxidize and absorb products of incomplete combustion. When the escaping bomb gases in each experiment were tested for carbon monoxide, using a NBS colorimeter method [22], only negligible traces of carbon monoxide were found.

2. Results

Table 5 gives the results of the heat of combustion measurements, where $-\Delta U_B$ is the observed heat of combustion under the conditions specified by the volume of the bomb (381 ml), the mass of water (1 g) placed in the bomb and the data given in columns 1 and 3; and $-\Delta U_C^\circ$ represents the decrease in intrinsic energy accompanying the combustion reaction when the components of the reaction are in their appropriate thermodynamic standard states at 30° C.

Except for the first experiment, in which the weight of the sample was apparently in error, the values obtained for the masses of carbon dioxide formed in the combustion are lower than the corresponding values calculated stoichiometrically from

TABLE 5. *Heat of combustion of diphenyl ether*

Defined calorie=4.1840 abs j

Mass of sample	Initial O_2 pressure at 30° C	Mass of CO_2	Heat of combustion at 30° C	
			$-\Delta U_B$	$-\Delta U_C^\circ$
Burned in platinum crucible				
g	*atm*	*g*	*abs j/g* CO_2	*abs j/g* CO_2
1.13560	31.1	3.52667	11613.33	11606.00
1.08319	30.4	3.35893	11616.98	11609.84
1.09104	30.4	3.38367	11620.74	11613.59
Burned in glass bulb				
1.12596	31.4	3.49271	11613.26	11605.87
1.10658	30.3	3.43144	11616.85	11609.68
0.99321	30.2	3.08082	11612.05	11605.06
Mean				11608.06
Standard deviation of the mean [a]				±1.34

	kj/mole	*kcal/mole*
$-\Delta U_C^\circ$ (*l*, 30° C)	[b] 6130.60 ±0.88	[b] 1465.25 ±0.21
$-\Delta H_C^\circ$ (*l*, 30° C)	[b] 6135.64 ±0.88	[b] 1466.45 ±0.21
$-\Delta H_C^\circ$ (*l*, 25° C)	[b] 6136.36 ±0.88	[b] 1466.63 ±0.21
$-\Delta H_C^\circ$ (*c*, 25° C)	[b] 6119.24 ±0.88	[b] 1462.53 ±0.21

[a] Standard deviation of the mean as used above is defined as $[\Sigma d^2/n\,(n-1)]^{1/2}$; where d is the difference between a single observation and the mean, and n is the number of observations.

[b] The value following the ± sign is a measure of the precision of the result, which is defined as follows [23]:

$$s=Q\sqrt{(s_E/E)^2+(s_Q/O)^2+(s_B/B)^2+(s_R/R)^2}.$$

In this expression, s_E is the standard deviation of the mean of the results of the series of experiments with benzoic acid to determine E, the energy equivalent of the calorimetric system; s_Q is the standard deviation of the mean of the results of the series of experiments to determine the heat of combustion, O, of the diphenyl ether; s_B/B is an allowance of 5×10^{-5} for the standard deviation of the value used for the heat of combustion of benzoic acid; s_R/R is an allowance of 5×10^{-5} for the standard deviation associated with the determination of the amount of the combustion reaction from the mass of carbon dioxide formed.

the masses of the sample burned. Excluding the first experiment, the average difference between the observed and calculated masses of carbon dioxide is 0.05 percent. The masses of carbon dioxide formed in the combustion of NBS Standard Sample 39f, benzoic acid, before and after the work with diphenyl ether agreed with the calculated values on the average within 0.010 percent. The low experimental value for the carbon dioxide formed in the combustion of diphenyl ether is probably due to air and water absorbed by the sample before the combustion experiment was made. These impurities have practically no effect on the value obtained for the heat of combustion per gram of carbon dioxide formed.

In table 5 are listed the values obtained for the heat of combustion per mole of liquid diphenyl ether at 30° C and of both liquid and solid at 25° C. The calculations were based on the mass of carbon dioxide formed in the combustion reaction, using the mean $-\Delta U_C^\circ$ per gram of carbon dioxide given in the same table and the value 44.010 g for the molecular weight of carbon dioxide. The results at 25° C were obtained, using the values of heat capacity and heat of fusion of diphenyl ether obtained in this work, together with the values of the heat capacity of gaseous carbon dioxide and oxygen and liquid water given in references [9, 24].

VI. Derived Thermal Properties

1. Enthalpy and Entropy

In table 4, columns 3 and 4, the values of enthalpy and entropy, respectively, are tabulated at integral temperatures for intervals of 2 deg from 0° to 50° K, 5 deg from 50° to 300° K, and 10 deg from 300° to 570° K. For most purposes any intermediate values can be obtained by linear interpolation or more accurately by quadratic interpolation. These properties were obtained by evaluating the thermodynamic relations

$$H_{\text{sat.}}-E_0^s=\int_0^T C_{\text{sat.}}dT+L_f+\int_0^T V_{\text{sat.}}\left(\frac{dp}{dT}\right)_{\text{sat.}}dT, \quad (8)$$

$$S_{\text{sat.}}-S_0=\int_0^T \frac{C_{\text{sat.}}dT}{T}+\frac{L_f}{T_t}, \quad (9)$$

where E_0^s is the internal energy of the solid diphenyl ether at absolute zero to which the enthalpy values are referred. S_0 is the entropy of the solid at absolute zero, which is considered to be zero for diphenyl ether. The other symbols have the same significance as previously indicated. The term $\int_0^T V_{\text{sat.}}(dp/dT)_{\text{sat.}}dT$ in the enthalpy equation was not applied up to 360° K; even at 570° K, the contribution from this term is only 0.03 percent. The term L_f (heat of fusion) in both expressions obviously is not applicable below the triple point. Below 18° K eq 8 and 9 were evaluated analytically, using the Debye heat capacity function given in eq 3. Between 18° and 570°K these equations were evaluated by tabular integration, using Lagrangian four-point integration coefficients. When the enthalpy values from tabular integration were checked in the interval from 370° to 570° K by evaluating the enthalpy eq 5, the discrepancy was found to be only 3 abs j mole^{-1}. No attempt was made to fit the tabulated values of heat capacity, enthalpy, or entropy between 18° and 370° K to an equation. The internal consistency of tabular integration in this lower temperature range, however, was checked by evaluating the thermodynamic identity:

$$\int_0^T (S_{\text{sat.}}-S_0)dT=T(S_{\text{sat.}}-S_0)-\int_0^T C_{\text{sat.}}dT-L_f. \quad (10)$$

Considering the accuracy claimed for the heat-capacity values and the uncertainty involved in the Debye extrapolation, a probable error of ±0.2 percent is assigned to the tabulated values of enthalpy above 50° K and a probable error of ±0.4 abs j deg^{-1} mole^{-1} to entropy in the whole temperature range.

2. Standard Heat of Formation

The standard heat of formation for both liquid and solid diphenyl ether at 298.16° K was calculated from the values of standard heat of combustion for this

material listed in table 5 and from the accepted standard heat of formation for liquid water ($-285{,}840\pm42$ abs j mole^{-1}) and carbon dioxide ($-393{,}513\pm45$ abs j mole^{-1}) [24] by evaluating the relation:

$$\Delta H_f^\circ = \Sigma \Delta H_f^\circ \text{ (products)} - \Delta H_c^\circ, \quad (11)$$

where ΔH_f° is the standard heat of formation; and $\Sigma \Delta H_f^\circ$ (products) is the sum of the standard heats of formation for the products of the combustion reaction. The results so obtained are given by

$$\text{Solid, } \Delta H_{f_{298.16^\circ K}}^\circ = -32.11 \pm 0.93 \text{ abs kj mole}^{-1}\ ^5$$

$$\text{Liquid, } \Delta H_{f_{298.16^\circ K}}^\circ = -14.99 \pm 0.93 \text{ abs kj mole}^{-1}\ ^5$$

3. Standard Entropy of Formation

The standard entropy of formation for solid diphenyl ether at 298.16°K was computed from the standard entropies of diphenyl ether (table 4), graphite (5.720 ± 0.050 abs j deg^{-1} mole^{-1}), gaseous hydrogen (130.574 ± 0.010 abs j deg^{-1} mole^{-1}), gaseous oxygen (205.073 abs j deg^{-1} mole^{-1}) [25] by evaluating the expression:

$$\Delta S_f^\circ = S_C^\circ - \Sigma S_E^\circ, \quad (12)$$

in which ΔS_f° is the standard entropy of formation; and the subscripts C and E indicate the compound and the element, respectively. The standard entropy of formation for diphenyl ether so obtained is

$$\Delta S_{f_{298.16^\circ K}}^\circ = -590.1 \pm 0.5 \text{ abs j deg}^{-1} \text{ mole}^{-1}.$$

The assigned probable error was estimated from the probable errors in the standard entropy for diphenyl ether and the elements.

Actually, in carrying out the above calculation the tabulated entropy (table 4) was used directly without correcting to standard state. The amount of this correction can be obtained using the following thermodynamic expression:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \quad (13)$$

There are no data for the temperature coefficient of expansion for solid diphenyl ether around 298° K, consequently the densities of solid diphenyl ether at 20° C and the liquid at 30° C [26] were used to calculate the maximum possible correction. This correction amounts to 0.02 abs j deg^{-1} mole^{-1}, which does not significantly affect the value of standard entropy of formation.

[5] The precision was determined by evaluating the expression:

$$s = \sqrt{(12 s_1)^2 + (5 s_2)^2 + (s_3)^2}$$

where s_1 and s_2 are the standard deviations of the mean of the heat of combustion values for carbon dioxide and water, respectively. s_3 is the precision s given in footnote b, table 5.

4. Standard Gibbs Free Energy of Formation

The standard Gibbs free energy of formation for solid diphenyl ether at 298.16° K was obtained from the values of standard heat and entropy of formation given in previous sections by evaluating the relation:

$$\Delta F_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ. \quad (14)$$

The value so obtained is

$$\Delta F_{f_{298.16^\circ K}}^\circ = 143.8 \pm 0.9 \text{ abs kj mole}^{-1}.$$

The probable error of ±0.9 abs kj mole^{-1} was obtained from statistical combination of the probable errors assigned to the various data used in the calculation.

VII. Discussion

The results of the purity determination indicate that diphenyl ether can be prepared in a state of extremely high purity. This material can be purified quite easily by slow fractional crystallization at room temperature. There is the question of chemical stability with the adiabatic vacuum calorimeter, but the heat of fusion results with the ice calorimeter indicate that even after several hours at 570° K in contact with monel the impurity increased by only 0.00002 mole fraction. No conclusion can be drawn without additional data in regard to the chemical reactivity of diphenyl ether with different metals.

There is implied in one set of enthalpy experiments (table 3) with the ice calorimeter that perhaps conditioning of the diphenyl ether crystal might affect the results of the experiments. The results indicate that the enthalpy is slightly lower for the material when cooled in dry ice. This difference is, however, so small that it is difficult to ascertain whether the effect is real or not. The experiments in the solid range with the adiabatic vacuum calorimeter do not indicate any unusual discrepancy in the results, although the material was subjected to extreme treatments such as freezing rapidly with liquid air and freezing slowly across a vacuum with ice. In the melting-point studies the diphenyl ether required relatively long periods for temperature equilibrium. This, however, is not uncommon with compounds of high molecular weight.

The results of the heat capacity experiments indicate that diphenyl ether is a suitable standard to be used in heat capacity calorimeters below 600° K. It might be possible to use this material above this temperature, but the increase in vapor correction would be undesirable. The material should be provided freed of air and water in ampoules of suitable volume.

As indicated by the 0.05-percent discrepancies in the weighed carbon dioxide from the stoichiometric value, the solubility of air and water in diphenyl ether is relatively high, for there is incomplete

combustion. Considering the difficulties involved in preventing the test material from being exposed to the atmosphere in combusiton calorimetry, diphenyl ether is undesirable as a combustion standard.

The authors express their indebtedness to several members of the Bureau—to F. L. Howard for purifying the diphenyl ether, to R. B. Scott for many helpful suggestions in the use of the adiabatic vacuum calorimeter, to T. B. Douglas and Anne F. Ball for help in taking the measurements and calculating the results with the ice calorimeter, and to R. S. Jessup for many suggestions and help with the combustion bomb calorimeter.

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